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OF URANIUM OXIDES

By

V. N. Strekalovskiy, A. P. Bessonov, V. G. Vlasov
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PHASE TRANSFORMATIONS DURING OXIDATION-REDUCTION OF URANIUM OXIDES

**V. N. Strekalovskiy, A. F. Bessonov, V. G. Vlasov, and
F. A. Sidorenko**

Conclusions pertaining to phase transformations in the uranium-oxygen system are given in this work based on the kinetic investigations of the reduction and oxidation processes of uranium oxides supplemented by an X-ray diffraction study of the products obtained.

The possibility of using the oxides of uranium (particularly the dioxide) as a ceramic nuclear fuel has attracted investigators to study the uranium-oxygen system in recent years.

Attempts are presently being made to construct the phase diagram of this system in a wide temperature range (from 0 to 1500°K) and components (U-UO₃) /1-3/. These endeavors are based mainly on studies of the oxidation or thermal decomposition of the oxides of uranium. Almost no data are to be found in the literature concerning phase transformations in reduction processes (especially in reference to the higher oxides of uranium).

Studies on reduction of uranium oxides with hydrogen are mainly devoted to a determination of the optimal temperature of reduction to obtain a dioxide of a stoichiometric composition. If we take into account the fact that the reduction processes of uranium oxides with hydrogen or with decomposed ammonia entered into the main manufacturing cycle of the last stages of uranium production /4/, then the appearance of works devoted to the mechanization of the reduction process is fully understandable /5, 6/. We also note that a number of works /7/ on this problem are in the stage of formulation.

We studied the kinetics of the reduction of amorphous UO_3 and the green form U_3O_8 with hydrogen in the 300-700°C range, and also the oxidation of UO_2 in atmospheres of air, oxygen, and carbon dioxide in the 165-860°C range, as well as the phase transformations taking place during the aforementioned processes. The Debye-Scherrer method was used for the X-ray crystal analysis. The Debye powder patterns were obtained for cobalt radiation of a BSV tube under operating conditions of 10 ma, 30 kv in the RKD and VRS cameras (magazine diameters of 57.3 and 143 mm). Uranium trioxide was prepared by roasting uranium peroxide $\text{UO}_4 \cdot n\text{H}_2\text{O}$ in a stream of oxygen at 350°C for five hours with a subsequent additional hour roasting at 400°C /8/.

Dark green mixed oxides were obtained by roasting the peroxide in air at 600°C /9/. Chemical analysis of the oxygen content showed that the composition of the product obtained corresponds to the formula $\text{UO}_{2.67}$.

In our study of oxidation the object was the inactive form of uranium dioxide, i. e., stable in air at room temperature. It was obtained by reduction of the mixed oxides of uranium with hydrogen at 800°C. The oxide composition on storage in air was $\text{UO}_{2.04}$. The orange UO_3 was amorphous, which agrees

with the data cited in the work on the study of U-O in the composition range of $UO_3 - U_3O_8$ /10/. The U_3O_8 had a hexagonal lattice similar to the structure obtained on roasting pitchblende at 400-500°C /11/. The starting dioxide had a cubic structure.

Results and Discussion

The diagram of the kinetic picture of the reduction processes of the higher oxides of uranium with hydrogen is shown in Fig. 1. It stands to reason that the value of the reduction rates of U_3O_8 and UO_3 , as well as the heights of the kinetic barriers during crystallochemical transformations of these oxides were dissimilar. The reduction of UO_3 with hydrogen begins at 350°C, whereas the temperature at the start of reduction of U_3O_8 corresponds to 450°C. It is necessary to note that under our experimental conditions the reduction of UO_3 at temperatures below 500°C practically ended on obtaining an oxide of the composition $U_{2.33}$; at higher temperatures the end product of reduction was U_4O_9 and products with a smaller content of oxygen.

When the mixed oxides (higher and lower) were reduced in the 450-700°C range, the composition of the end products was in the range $UO_{2.18} - UO_{2.08}$.

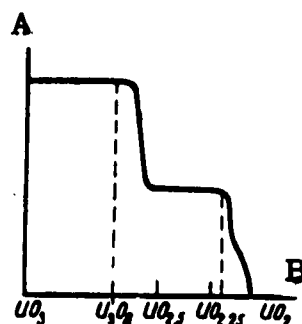


Fig. 1. Diagram of the kinetics of the reduction process of the higher oxides of uranium with hydrogen: A) rate of process (in conventional units); B) total composition of the solid reduction product (O/U ratio)

The X-ray pictures of the end products obtained by reduction of U_3O_8 with hydrogen to various stages of deoxidation are shown in Fig. 2. The kinetic and X-ray data permit the conclusion that the following phase transformations are present during reduction of mixed uranium oxides.

At first there occurs an oxygen-depletion of the uranium mixed oxides. According to the phase diagram, /1/ this process can continue until a solid phase of composition $UO_{2.56}$ is obtained. The abrupt drop in the reduction rate (see Fig. 1) until this composition is reached can be due to the difficulty in removing the last portions of oxygen from the solid phase and by the difficulty in forming nuclei of the new phase which has different crystal lattice.

At 46.9% reduction, which corresponds to the total composition of the solid phases $UO_{2.539}$ (taking the complete change of UO_3 to UO_2 as 100% reduction), the U_3O_8 lines are retained on the X-ray picture. Only the parameters of the starting lattice vary; the lines of the new phase are not observed.

The lines of the starting oxide are still retained at 62 and 69% reduction, and the lines of the cubic phase U_4O_9 appear. At 75% reduction the lines of the mixed oxides completely disappear and only the lines of the cubic lattice of the β -dioxide (U_4O_9) remain. On further deoxidation the lattice remains cubic and only its parameters are increased.

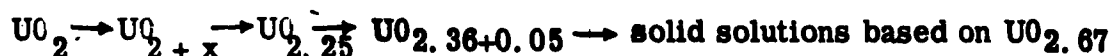
The reduction of uranium trioxide proceeds analogously; it is only necessary to note that during reduction of amorphous trioxide the mixed oxides are formed without preliminary crystallization of the starting oxide.

In the work mentioned above /6/ the equilibrium of uranium oxides produced by reduction of the mixed uranium oxides with a mixture of $H_2 + H_2O$ in the 400-600°C range, no phases were detected other than the solid solution of the type U_3O_8 , U_4O_9 (β), and UO_2 (α). It was simultaneously noted that the region where α - and β -phases coexist is expanded when the temperature drops. It was shown in the literature /3/ that the reduction of U_4O_9 with hydrogen in the same temperature ranges proceeds with the formation of the nonstoichiometric compound UO_{2+x} . Since the formation of the phases U_4O_9 and UO_{2+x} takes place by the ordered (in the first case) and disordered (in the second) introduction of oxygen into the cubic lattice of the uranium dioxide /12/, then on reduction of the U_4O_9 we can expect that the cubic structure will be retained (mixtures of U_4O_9 and UO_{2+x} will be formed). The diffuse lines at large reflection angles attest to the formation of these mixtures for the reduction products in the composition range of $UO_{2.08} - UO_{2.15}$.

Thus the phase transformation taking place during the reduction of UO_3 and U_3O_8 with hydrogen in the investigated temperature range can be represented by the following scheme:

$\text{UO}_3 \rightarrow \text{solid solutions based on } \text{UO}_{2.67} \rightarrow \text{UO}_{2.25} \rightarrow \text{UO}_2 + x.$
amorphous

Kinetic investigations on the oxidation of uranium dioxide with pure oxygen and atmospheric oxygen were supplemented by an X-ray analysis of the products at various stages of oxidation. On the basis of these data the scheme of the phase transformations in the 260-340°C range has the following form:

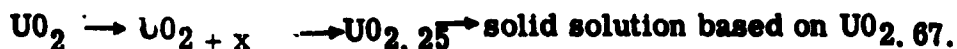


From the point of view of the structural changes, in the first two stages oxygen is introduced into the cubic lattice of the uranium dioxide.

The kinetic characteristics show the existence of a number of tetragonal phases: $\text{UO}_{2.32+0.01}$; $\text{UO}_{2.34}$; $\text{UO}_{2.37}$ and $\text{UO}_{2.41}$, which agrees with the data of other investigators [2, 3]. However, the X-ray diffraction analysis of them can be carried out only on freshly prepared specimens since a decomposition of the tetragonal phase to U_4O_9 and U_3O_8 occurs with time.

The physical picture of the last stage can be given within the frameworks of the processes of the formation of nuclei of the new phase (U_3O_8) and their further growth. A hexagonal form of U_3O_8 is the end result of oxidation.

The tetragonal phase does not form at temperatures above 400°C, even as a labile intermediate product, and therefore the scheme of the phase transformations on oxidation in the 400-860°C range has the form



Hexagonal mixed oxides of uranium are the upper limit of the solid solution based on $\text{UO}_{2.67}$.

Carbon dioxide does not oxidize uranium dioxide: the crystal lattices of the dioxide exposed to CO_2 at 860°C and the UO_2 obtained by the reduction of U_3O_8 with hydrogen at 800°C in no way differ from each other (Fig. 3).

Conclusions

1. The kinetic investigations of the reduction processes of the higher oxides of uranium (UO_3 and U_3O_8) with hydrogen were supplemented by an X-ray analysis of the reduction products. In all cases no other types were formed except the solid solutions based on U_3O_8 , U_4O_9 , and UO_2 .
2. Tetragonal phases formed only at temperatures below $400^\circ C$ in the oxidation processes of uranium dioxide with pure oxygen and atmospheric oxygen.
3. The X-ray analysis confirmed that uranium dioxide is not oxidized in a CO_2 atmosphere.

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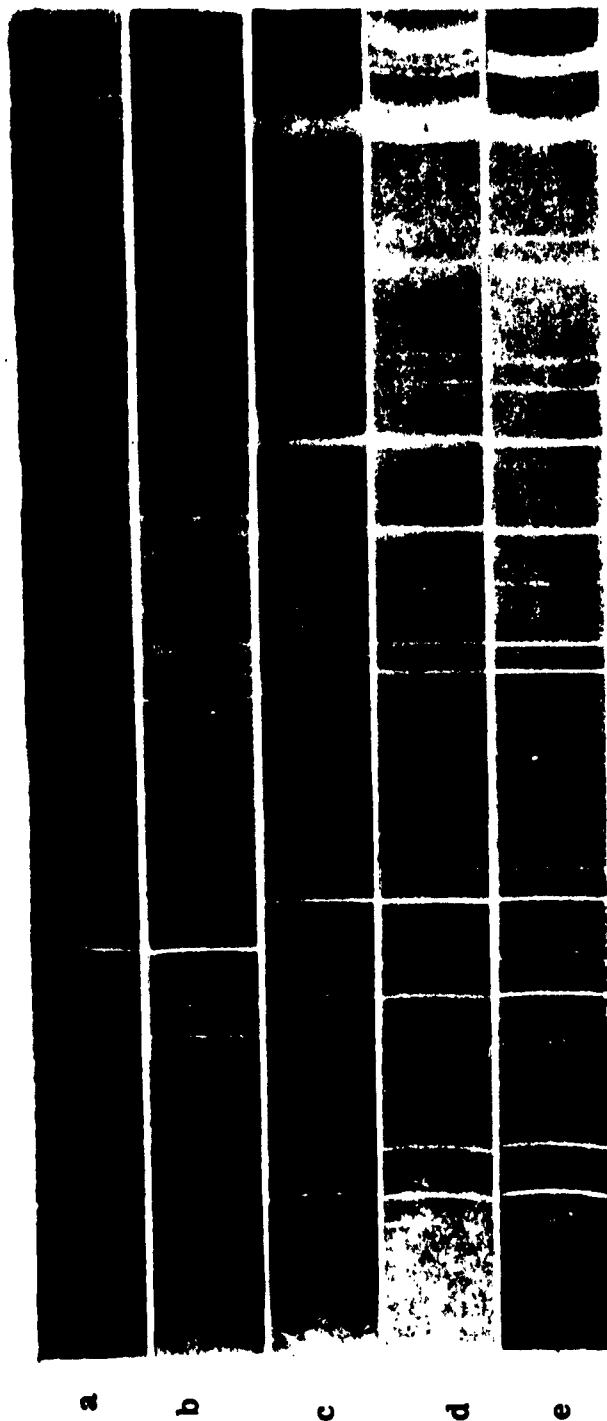


Fig. 2. X-ray pictures of the various stages of the reduction of U_3O_8 with hydrogen (total conversion of UO_3 to UO_2 taken as 100% reduction): a) starting U_3O_8 33.3% reduction; b) 45.9% reduction; c) 69% reduction; d) 85.8% reduction; e) 88% reduction.



Fig. 3. X-ray picture of uranium dioxide obtained by the reduction of U_3O_8 with hydrogen at $800^\circ C$.

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